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Complete coverage of reduced graphene oxide on silicon dioxide substrates*

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Reduced graphene oxide (RGO) has the advantage of an aqueous and industrial-scale production route. No other approaches can rival the RGO field effect transistor platform in terms of cost (<US$1) and portability (millimetre scale). However the large deviations in the electrical resistivity of this fabricated material prevent it from being used widely. After an ethanol chemical vapor deposition (CVD) post-treatment to graphene oxide with ethanol, carbon islets are deposited preferentially at the edges of existing flakes. With a 2-h treatment, the standard deviation in electrical resistance of the treated chips can be reduced by 99.95%. Thus this process could enable RGO to be used in practical electronic devices.

Keywords: graphene oxide, reduced graphene oxide, graphene growth, field effect transistor

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1. Introduction

For the successful commercial development of disposable sensors, a low-cost industrial-scalable yet sensitive transducer is required.[1,2] Reduced graphene oxide (RGO) fits these descriptions,[3] however, the large deviations in the electrical resistivity of this fabricated material prevent it from being used widely.[4] This deviation is caused by the heterogeneous and incomplete coverage of RGO on the fabricated surfaces. The limitation could be solved by growing RGO to obtain complete coverage of the transducer on silicon dioxide surface using ethanol chemical vapor deposition (CVD) as presented in this paper. Additionally this process can be easily employed by the semiconductor manufacturers as it is compatible with existing techniques in the industry.

2. Experimental methods

2.1. Sample preparation

Graphene oxide (GO) flakes, to be used as growth templates, were obtained using a modified Hummer's method as reported previously.[5] Large graphite flakes of 3–5 mm were pre-oxidized using ultra-sonication in concentrated sulphuric acid. Then, the pre-oxidized graphite powder was further oxidized by using a mixture of concentrated sulphuric acid and potassium permanganate. Hydrogen peroxide was used to stop the reaction to obtain a stock solution of large GO flakes. Thereafter, the GO solution was drop-casted onto 3-aminopropyltriethoxysilane (APTES) functionalized silicon dioxide (SiO_2) chips (1.5 cm × 1.5 cm). The initial coverage of GO on APTES-SiO_2 chips ranged from 60%–90% due to the cross-linkage of APTES, the varying shapes of the GO flakes, as well as the delamination during the rinsing process. The SiO_2 chips, with the single/double layered of GO flakes electrostatically attached, were then placed into an ethanol CVD setup.[6]

2.2. CVD synthesis

A CVD tube furnace was purged with argon gas for more than 30 min to remove any remaining oxygen which could oxidize GO into its by-products. During the CVD treatment, argon and hydrogen gas were set at 100 sccm and 20 sccm respectively. The gases were bubbled through an ethanol bubbler with the temperature kept constant at 0 °C. The furnace was then set at 950 °C, similar to the carbon nanotube growth setup. After a 1-hour treatment, the heater was turned off and the furnace was left to cool to room temperature with the gas flow on. The treated RGO were characterized with (i) a JEOL JSM-7600F field effect scanning electron microscope (SEM) operating in gentle beam mode at 1 kV or in scanning transmission electron microscopy (STEM) mode at ∼ 15 kV;[7,8]

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(ii) thermo scientific VG ESCA 220i-XL imaging X-ray photoelectron spectroscopy (XPS) operating with an Mg Ka X-ray source and analyzing with a photoelectron take-off angle of 90° with an area of about 4 mm × 4 mm; (iii) transmission electron microscope images taken using a JEM-2100F instrument operating at 200 kV.

3. Results and discussion

After a 2-h ethanol CVD treatment, the entire substrate is completely covered with the RGO flakes and RGO new growth. Figure 1(a) shows the substrate before growth and figure 1(b) shows the substrate after growth. The extended growths are lighter in tone in comparison with the existing GO flakes because of the e-beam-induced surface potential between graphenes of different band-gaps.[9]

To further elucidate the growth process, a higher magnification image is taken after a 30-min ethanol CVD treatment (Fig. 1(c)). At this stage, the substrate is only partially covered with the newly grown RGO flakes. Carbon islets are observed to deposit preferentially at the edges of template flakes. Clean substrates without GO are also ethanol CVD treated for up to 2 hours and no growth is observed. Thus GO acts as a catalyst at preferential growth sites for RGO new growths. The two-dimensional electron gas properties of GO that are similar to that of the metal surface could help to catalyse the RGO new growths in the ethanol CVD treatment.

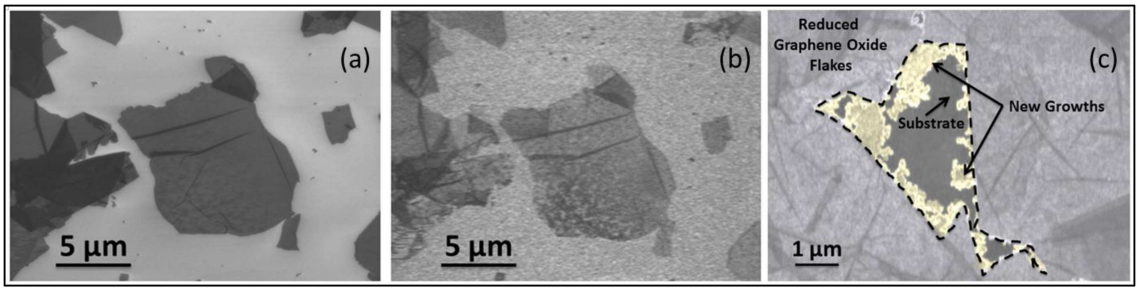


Fig. 1. SEM images of (a) GO flake templates on SiO_2 substrate, before ethanol CVD treatment; (b) RGO flake with RGO new growths completely covering substrate, after a 2-hour CVD treatment; (c) high-magnification image of the newly grown flakes bridging a gap between RGO flakes.

The C1s spectra of RGO shown in Fig. 2 can be deconvoluted using Lorentzian with Gaussian broadening curve-fitting into C=O (∼ 287.2 eV), C–OH (∼ 286.3 eV), and C–C (284.5 eV). These values are in agreement with previous reports.[6,10,11] The C–C spectrum peak positions for all five samples are all detected to be at 284.5 eV. However, there are variations in C=O and C–OH spectrum peak positions for different samples. The sample treated with more hydrogen gas has both C=O and C–OH down-shifted, followed by the sample with standard CVD treatment, CVD treatment with no ethanol, hydrazine treatment, and graphene oxide. The CVD treatment with more hydrogen has a big chemical shift towards that of highly ordered pyrolytic graphite (HOPG), which indicates that the bonds present in the compound are more similar to those of HOPG. This shows that the presence of hydrogen gas in the ethanol system could act as an etchant which can anisotropically etch amorphous carbon to produce reduced graphene oxide closer to that of HOPG, similar to what has been reported for graphene systems.[12] Hydrogen also preferentially etches away stacked carbon (16 kJ/mol) and possibly some oxygen moieties due to the weak bond compared with in-plane carbon (345 J/mol) thus leading to more graphitized RGO instead of amorphous carbon.[13] The atomic percentages of the bonds present in the XPS spectra are then calculated and presented in Table 1.

In all the RGO samples, the atomic percentages of C–OH bonds decrease while the percentages of C–C bonds increase. For the sample with standard CVD treatment, the C=O bond peak (initially at 2.4%) is completely removed indicating an efficient graphitization. The C=O bond in the CVD treatment can be reduced into a C–O bond, a reduced species of C=O.[6] However, in other reduced samples, the atomic percentage of C=O bonds increases. This is not in agreement with the results in the existing literature:[4,10,14] this could be due to the initial large GO flakes used. With larger GO flakes, the atomic percentages of both C=O and C–OH, which are predominantly found at the edges of the flakes, are much lower in our reported GO than in the GOs synthesized in the existing literature.[3,10,15]

The remaining C=O bonds and higher atomic percentage of the C–OH bonds indicates that the presence of ethanol, and the right flow rate of hydrogen gas are critical in the complete and efficient graphitization of RGO. The CVD procedures, gas flow parameters, and ethanol setup used in this study are optimized for growing carbon nanotubes cleanly without amorphous carbon. Deviation from the optimal condition can result in residual C=O bonds. Using CVD treatment of no ethanol but more hydrogen or using hydrazine treatment results in RGO products with a similar C–C bond percentage (∼ 69%), but with different percentages of C–OH and C=O bonds, which are dependent on the condition used. With 1-h CVD treatment, the C–C bond percentage increases to 82.8%. As a result, tailoring of RGO products with specific bonds could be realized by adjusting the reaction conditions.

Table 1. Atomic percentages of different carbon bonds identified by XPS on mono-layered GO and RGO reduced under different conditions.

Samples	C=O /(atomic %)	C–OH/(atomic %)	C–C/(atomic %)
Graphene oxide	2.4	38.7	58.9
CVD treatment: standard	0	17.2	82.8
CVD treatment: no ethanol	9.8	21.2	69.0
CVD treatment: more hydrogen	12.5	18.2	69.3
Hydrazine treatment	5.4	25.8	68.8

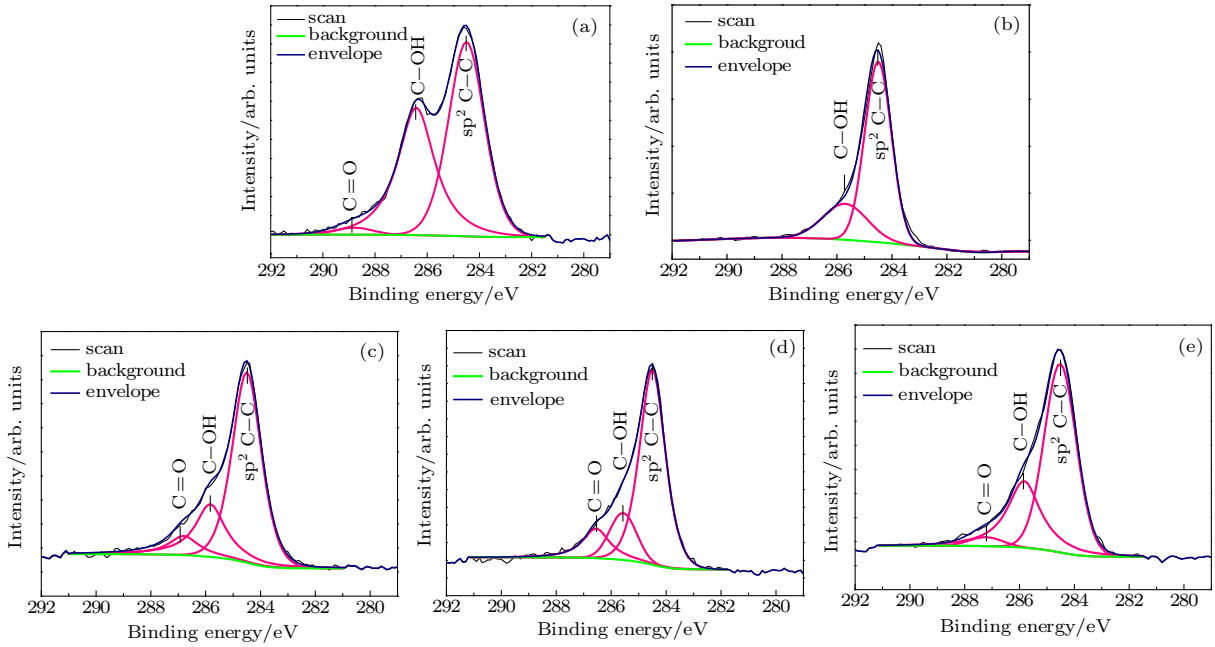


Fig. 2. (color online) C1s XPS spectra (hv = 1486.6 eV) collected on (a) graphene oxide; and reduced graphene oxide reduced in a similar CVD setup with (b) 1-h standard CVD treatment, (c) 15-min CVD treatment with no ethanol, (d) 1-h CVD treatment with more H_2 gas, (e) 12-h hydrazine-reduced sample. The different components related to various chemical shifts of carbon bonds are indicated.

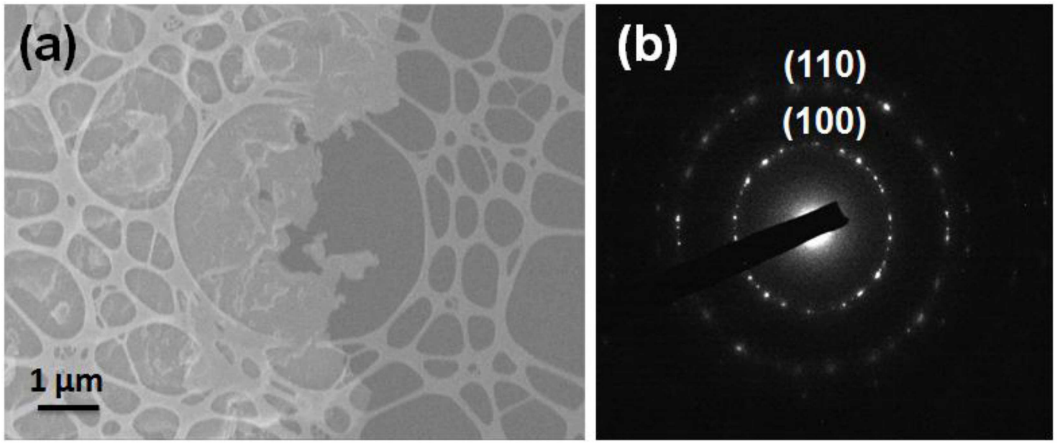


Fig. 3. (a) Electron microscope image and (b) SAED patterns of 2-h treated graphene oxide on lacey carbon.

Figure 3(a) shows the electron microscope image of free-standing reduced graphene oxide after 2-h CVD treatment. Figure 3(b) shows the selected area electron diffraction (SAED) of the same sample, and the patterns match those expected of few layered graphene-based sheets.[16,17] The well-defined diffraction spots in SAED also indicate that the structure of the reduced graphene oxide has an internal ordered crystalline structure after the CVD treatment. However, after a minute of exposure to the electron beam during the TEM observation, the reduced graphene oxide is vaporized, which is possibly caused by the evaporation of the hydrogen and oxygen-containing functional groups still existing on the reduced graphene oxide.

The electrical resistivity values of 2-h CVD treated samples are then measured using a 4-point probe. The average resistance is 4681 Ω/square, and the electrical resistance stan-

dard deviation is only 770 Ω/square. In comparison, the GO treated with 12-h hydrazine vapor has an average electrical resistance of 1.99×10^6 Ω/square and a standard deviation of 1.60×10^6 Ω/square. Thus ethanol CVD treatment can reduce both electrical resistance (99.75%) and its standard deviation (99.95%) drastically. Research on the mechanism of the RGO growth is currently in progress. Eventually, this RGO growth can be used to fabricate biosensor transducers for the study of important molecules such as Interleukin-6 (IL6).[18]

4. Conclusions

A complete coverage of reduced graphene oxide on silicon dioxide substrate which exhibits considerably lower electrical resistance and standard deviation is fabricated and characterized. A 2-h CVD ethanol treatment can reduce both electrical resistance (99.75%) and its standard deviation (99.95%) drastically, thus enabling RGO to be used in practical FET platforms for low-cost and portable electronics such as biosensors, which may have important implications for reducing the time delay in medical diagnostics.

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